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<sup>\*</sup> ye initially, after vowels, and after \( \bar{\pi} \), \( \bar{\pi} \) e elsewhere. When written as \( \bar{\pi} \) in Russian, transliterate \( \bar{\parabox} \) s \( \bar{\pi} \) or \( \bar{\pi} \). The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

### INVESTIGATION OF CARBIDE REGION OF Ta-Hf-C SYSTEM

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Investigation of TA-Hf-C system in the carbide region presents definite interest due to high refractoriness of tantalum and hafnium monocarbides. It could be expected that combinations of these carbides will have still higher melting points, which is confirmed by source material about the melting point of complex carbide 4TaC·HfC, equal to approximately 3942°C [1]. Results of investigation of binary systems Ta-C, Hf-C and HfC-TaC are published in [1-6].

Investigation of the carbide region of Ta-Hf-C system was proposed for alloys, compositions of which lie on sections TaC-HfC and Ta<sub>2</sub>C-HfC. However, because of the great volatility of carbon at high temperatures not all the compositions of prepared alloys fell on the above-indicated sections.

By methods of X-ray and metallographic analyses of alloys, quenched from temperature 2400 and 1500°C, and by measurement of their microhardness we studied isothermal sections of ternary system. For cast alloys we determined their temperatures of beginning of melting.

¹This work was done in 1961. In subsequent years there have been published works confirming our results [for example, Rudy E., Nowotny H. Monatsh. Chem., 94, 507 (1963)].

Initial materials for production of alloys were powdery tantalum (96.97 wt %), hafnium oxide (98.0 wt %) and spectrally pure carbon. All alloys were manufactured by pressing and sintering of specific quantities of initial materials at a temperature of 2000°C for 5 hours with subsequent remelting of sintered briquettes in an arc furnace in an atmosphere of pure argon. Chemical analysis of the obtained alloys is listed in the table, and their location on concentration triangle is shown on Fig. 1.

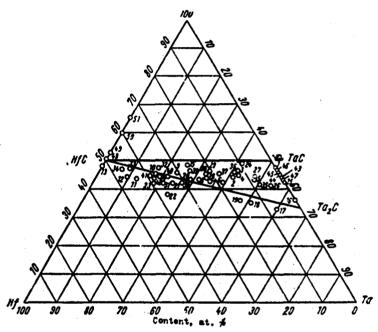


Fig. 1. Compositions of alloys of Ta-Hf-C system (at points there is shown the number of alloy).

Annealing of alloys with subsequent quenching was performed 1500 and  $2400^{\circ}$ C for 30 and 5 hours respectively in an atmosphere of purified helium. Temperatures of beginning of melting of alloys, determined with  $\pm 80^{\circ}$ C accuracy by the method described in [7], are listed in the table. For all prepared alloys the temperature of beginning of melting does not exceed the melting points of tantalum and hafnium carbides, although it is very high (3280-3840°C). In Hf-C system there was determined the melting point of eutectic between hafnium carbide and carbon, equal to  $3230^{\circ}$ C.

Composition, melting point and lattice parameter of  $\delta\text{-phase}$  of alloys of Ta-Hf-C system.

mete	er or	o-pn			•	or ra-	HI-C S	ystem.			
2	Composition of alloys according   Melting   Lattice   para										
No. of	wt. %			ат. %			point OC	meter of			
\$.9	Hf	Ta	c (	Hf	Ta	C	70	δ-phase,			
1 2 3 4 5 6	23,94 21,13 21,43 23,19 31,19	94,47 70,80 73,35 73,33 71,93 64,20	5,53 5,26 5,52 5,24 4,88 4,61	14,44 11,91 12,36 13,76 18,95	52,82 41,31 41,33 42,29 42,68 38,87	47,18 44,25 46,76 45,35 43,56 42,18	3680 3765 3540 3630 3685 3645	4,430 4,459 4,441 4,458 4,454 4,455			
7 8 9 10 11 12	36,91 42,53 52,47 63,63 74,13 79,45	58,30 52,59 42,20 31,03 20,98 15,48	4,79 4,88 5,33 5,34 4,88 5,07	22,14 25,19 29,96 36,34 43,99 46,43	34,76 31,25 24,16 17,72 12,45 9,05	43,10 43,56 45,88 45,94 43,56 44,52	3600 3575 3605 3715 3750 3540	4,477 4,507 4,496 4,566 4,594 4,601			
13 14 15 16 17 18	93,62 62,47 46,76  9,82 19,88	0,55 32,56 47,32 96,32 86,96 76,60	5,83 4,97 5,92 3,68 3,22 3,52	51,50 36,79 25,57  6,77 13,38	0,30 19,16 25,83 63,60 59,93 51,14	48,20 44,05 48,60 36,40 33,30 35,48	3845 3495 3560 3440 3420 3280	4,644 4,566 — — —			
19 20 21 22 23 24	24,39 46,88 55,19 57,29 64,34 16,67	71,99 48,30 40,15 38,71 31,03 73,28	3,62 4,82 4,66 4,00 4,63 6,05	16,17 27,90 33,27 36,71 38,83 9,07	47,71 28,84 24,29 24,79 18,75 41,71	36,12 43,26 42,44 38,50 42,42 49,22	3340 3280 3540 3345 3660 3760	-			
25 26 27 28 29 30	6,69 13,23 36,76 35,32 50,02	95,28 88,77 81,68 58,10 59,22 45,26	4,77 4,54 5,09 5,14 5,46 4,72	4,07 7,73 21,95 20,03 30,00	57,25 54,03 47,67 33,15 33,47 27,26	42,75 41,90 44,60 44,90 46,50 42,74	3730 3670 3680 3685 — 3770	4,418 4,432 4,459 4,482 4,505 4,512			
31 32 33 34 35 36	59,26 63,11 79,96 82,45 13,56 21,67	36,11 31,22 15,33 12,09 81,81 72,96	4,63 5,67 5,71 5,46 4,63 5,37	36,17 35,15 43,79 46,65 8,20 12,32	21,53 17,39 8,57 6,85 49,50 41,52	42,30 47,46 47,64 46,50 42,30 46,16	3680 3550 3670 3655 3690 3540	4,534 4,564 4,613 4,446 4,470			
37 38 39 40 41	30,91 37,65 46,48 57,80 65,99	63,77 57,07 48,24 37,11 28,92	5,32 5,28 5,28 5,09 5,09	17,69 21,66 26,78 33,56 38,48	36,47 32,72 27,60 21,80 16,88	45,84 45,62 45,62 44,64 44,64	3710 3630 3660 3665	4,488 4,504 4,528 4,542 4,562			
42 43 44 45 46 47	64,34	30,57 95,07 94,95 94,77 94,57 95,15	5,09 4,93 5,05 5,23 5,43 4,85	37,50	17,86 56,18 55,56 54,63 53,62 56,60	44,64 43,82 44,44 45,37 46,38 43,40	3350 3855 3800 3735 3785 3800	4,565 4,411 4,420 4,422 4,432			
48 49 50 51	93,59 93,13 90,90 88,80	-	6,41 6,87 9,10 11,20	49,26 47,28 40,00 34,82	-   -	50,74 52,72 60,00 65,18	3545 3510 3240 3220	-			

Note: According to chemical analysis, in alloy No 7 there is 3.0 wt. % tungsten, in alloy No. 8 - 2.5 wt. %.

Phase diagram of cast alloys of Ta-Hf-C system, compiled according to metallographic and X-ray analyses, is shown in Fig. 2.

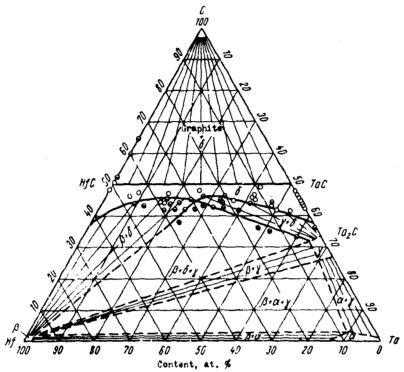


Fig. 2. Phase diagram of cast alloys of Ta-Hf-C system: O - single-phase alloy:  $\bullet$  - two-phase alloy;  $\bullet$  - three-phase alloy;  $\delta$ -phase - solid solution of hafnium and tantalum monocarbides;  $\beta$ -phase - solid solution of carbon and tantalum in hafnium;  $\gamma$ -phase - solution of hafnium in Ta<sub>2</sub>C.

On this diagram there are determined regions of existence of  $\delta$ -phase and partically the boundaries of two-phase regions  $(\beta + \delta)$  and  $(\gamma + \delta)$  and ternary region  $(\beta + \delta + \gamma)$ . Typical microstructures of alloys from these regions are shown on Fig. 3. In the table are listed lattice parameters of  $\delta$ -phase for the majority of cast alloys. As can be seen, parameter lattice of  $\delta$ -phase is increased with increase of the carbon content in it and with increase of the quantity of hafnium monocarbide.

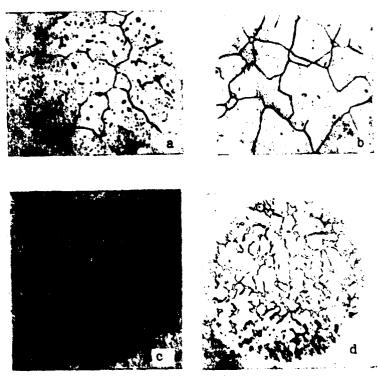


Fig. 3. Microstructure of cast alloys No. 12 (a), 15 (b), 30 (c), 6 (d) (×240).

On the basis of results of metallographic and X-ray investigations there is constructed isothermal section of ternary system Ta-Hf-C at  $1500^{\circ}$ C (Fig. 4). Comparison with the phase diagram of cast alloys shows that the region of existence  $\delta$ -phase was increased somewhat at the expense of decrease of region  $\beta$  +  $\delta$ ; furthermore  $\delta$  +  $\gamma$  was increased insignificantly. In two-phase region  $\beta$  +  $\delta$  there are located two single-phase alloys - No. 31 and No. 40, and in region  $\delta$  +  $\gamma$  - three phase alloy No. 7. Obviously, such a change of composition of samples is caused by inaccuracy of determination of the chemical composition of alloys, since chemical analysis was conducted only for cast alloys, and during annealing of samples under conditions of high temperatures the content of carbon could be changed because of its considerable volatility.

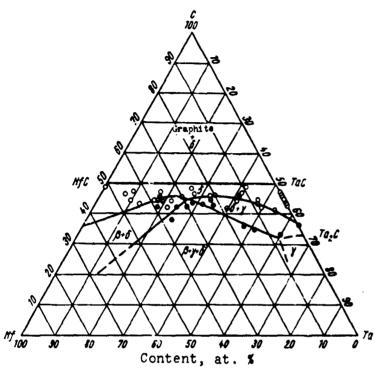


Fig. 4. Isothermal section of Ta-Hf-C system at 1500°C (see designations on Fig. 2).

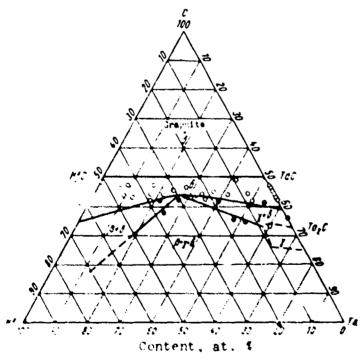


Fig. 5. Is thermal section of Ta-Hf-C system at 2403% (see perionations on Fig. 2).

Isothermal section of ternary system Ta-Hf-C at  $2400^{\circ}$ C (Fig. 5) basically coincides with analogous section at  $1500^{\circ}$ C. However, one should note the considerable increase of region of  $\delta$ -solid solution and some decrease of two-phase regions  $\beta + \delta$  and  $\gamma + \delta$ . Alloy No. 17 (see Fig. 1), which was two-phase in cast state and after annealing at  $1500^{\circ}$ C, became single-phase after annealing at  $2400^{\circ}$ C. In connection with this, we can expect that  $\gamma$ -region is expanded with increase of temperature, which for binary system Ta-C is confirmed by literature data.

### Conclusions

- 1. There is established the existence of complex carbide (Ta, Hf) C and there is determined the region of its homogeneity at high temperatures.
- 2. Complex carbide is very refractory (in investigated region of concentration the melting point is higher than 3200°C).
- 3. Melting point of eutectic in HfC-C system is lower than the melting point of eutectic in TaC-C system, and is  $3230^{\circ}$ C.
- 4. We can expect higher melting points for complex carbides, compositions of which correspond to quasi-binary section HfC-TaC.

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ABSTRACT

(U) Carbide combinations of the system Ta-Hf-C are of definite interest in view of their high melting points (e.g. the m.p. of the complex carbide 4TaC times HfC is approximately 3942 degrees centigrade). In this connection the carbide region of this system was investigated with respect to specimens of 51 different alloys whose compositions lie on the sections TaC-HfC and Ta(subscript 2)C-HfC of the constitution diagram. Isothermal sections of this ternary system were accordingly studied by methods of x-ray and metallographic analysis of alloys quenched from 2400 to 1500 degrees centigrade along with measurements of microhardness of these alloys. In all the investigated alloys the melting point did not exceed the melting points of the carbides of tantalum and hafnium, even though it was extremely high (3280-3840 degrees centigrade). A comparison of the isothermal section of the ternary system Ta-Hf-C at 1500 degrees centigrade with its counterpart at 2500 degrees centigrade showed no difference. It is shown that the lattice parameter increases with decrease in its C content and increase in its HfC content. The existance of the complex carbide (Ta, Hf)C is established and the region of its homogeneity at high temperatures is defined. The melting point of the eutectic in the system HfC-C is lower (3230 degrees centigrade) than the melting point of the eutectic in the system Orig. art. has: 1 table, 5 figures.